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(64) A method of preparing ceramic parts by electrophoresis

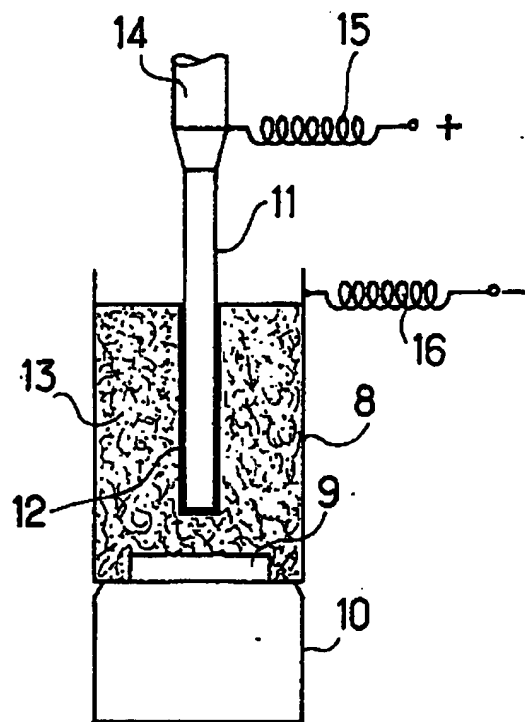
(57) The invention relates to a method of preparing ceramic parts and in particular beta sodium alumina parts. It consists in putting a ceramic powder in suspension in a polar solvent, depositing a layer of ceramic substance on a mandrel by electrophoresis while imparting to the mandrel a polarity which is the opposite of that of the powder, drying the layer, isostatically compressing the deposit, and removing the mandrel and sintering the part thus obtained; said solvent having, at a temperature substantially equal to ambient temperature, the following characteristics: — a viscosity of at most 2 centipoise; a boiling temperature of at least 60°C; a relative dielectric constant of between 12 and 22; and a saturated vapour pressure of at most 50 millimetres of mercury;

The invention can be used for preparing solid electrolytes used in sodium-sulphur electric cells.

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ORIGINAL

A method of preparing ceramic parts by electrophoresis

The present invention relates to a method of preparing ceramic parts, in particular by electrophoresis.

It is advantageously used for making parts, in particular tubes made of a solid electrolyte such as beta sodium alumina, such tubes being used in electric cells which operate at high temperatures, for example in sodium-sulphur electric cells.

It is known, in particular from the Applicants' first certificate of addition n° 95 549 to French patent n° 1 597 279, dated 27th December, 1968, entitled: "A method of producing thin parts made of a ceramic material", to prepare ceramic parts by electrophoresis in a way summarized substantially as follows:

10 A method of producing thin parts made of sinterable material, in particular a ceramic material, in which said material is deposited on a suitable support or mandrel, is put under pressure isostatically and is then subjected to a sintering treatment, the method being characterized by the following points:

1. Depositing is by electrophoresis, i.e. in a first step, the particles of sinterable material are treated in a suitable liquid so as to be electrically charged, then the charged particles in the suspension are deposited on 15 said mandrel or support which is immersed in the suspension while an opposite polarity to that of said particles is imparted to the mandrel, thereby establishing a difference in potential between the mandrel and, for example, a receptacle which contains the suspension.

2. Said liquid is constituted by nitromethane to which small quantities of benzoic acid have been added.

3. Said liquid may also be constituted by a mixture of acetone and of ethyl alcohol containing small 20 quantities of nitro-cellulose.

4. Firstly, particles of the sinterable material are added to a nitromethane solution, then, after mixing, benzoic acid is added thereto and a new mixture is formed.

5. The difference in potential between the mandrel and the receptacle which contains the suspension of charged particles of the sinterable material lies between 30 and 500 volts.

25 6. To produce tubes, a rotating cylindrical mandrel is used.

7. The porosity of the deposit can be adjusted according to the size of the particles of the sinterable material.

8. In order to increase the porosity of the deposit, porogenous compounds which disappear for example during sintering may be inserted in the deposit.

30 9. To increase the solidity of the deposit, a binding agent is added thereto.

10. The above-mentioned binding agent is diphenol polycarbonate.

11. The above-mentioned binding agent is ethyl cellulose.

12. The binding agent is added to the suspension of particles of material which can be sintered in the form of a solution.

35 13. The binding agent solution consists of chloroform which contains about 2 to 3 % by weight of diphenol polycarbonate.

14. The binding agent solution consists of carbon tetrachloride which contains about 2 to 3 % by weight of ethyl cellulose.

40 However, although parts obtained by the above method are of a quality which is improved in relation to those manufactured by prior methods, a number of disadvantages have been observed.

Firstly, the above liquid is relatively expensive, in particular because of the high price of nitromethane.

Further, it is appreciably volatile and hence slightly toxic; this leads to the use of installations for ventilating the premises in which it is used.

45 In conclusion, although such a liquid is suitable for use in a laboratory, it is not easy to use industrially because of the disadvantages listed hereinabove.

The Applicant has therefore produced another liquid or bath which does not have such disadvantages and which can therefore be used industrially.

50 Systematic testing has revealed that the viscosity, boiling point, dielectric constant and saturated vapour pressure of such a liquid should be well-determined so that it can be used in the method of the present invention.

The invention therefore provides a method of preparing ceramic parts, said method comprising the following successive stages:

— a powder of said ceramic substance is put in suspension in a polar solvent, having the following characteristics at a temperature substantially equal to ambient temperature: a viscosity of at most 2 centipoise, a boiling temperature of at least 60°C; a relative dielectric constant which lies between 12 and 22; and 55 a saturated vapour pressure of at most 50 millimetres of mercury.

— a layer of ceramic substance is deposited on a mandrel or support by electrophoresis by immersing said mandrel or support in said suspension and by imparting to said mandrel or support a polarity which is the opposite of that of said powder by setting up a difference in potential between the support and, for example, 60 the receptacle which contains said suspension,

— said layer is dried,

— the deposit obtained undergoes isostatic compression; and

— the part thus obtained is sintered after the mandrel has been removed.

65 An embodiment of the invention is described by way of example with reference to the sole figure of the accompanying drawing.

Firstly, beta sodium alumina powder which has a specific area of about $1 \text{ m}^2/\text{g}$ after crushing is put in a suspension by crushing in a polar solvent such as methylpropyl ketone or n-pentanol.

The concentrations of alumina lie between 100 and 1000 g per litre of solvent. For high proportions of alumina, chloroacetic acid may advantageously be added as a deflocculant, in a concentration of 1 to 5 g of acid per 1000 g of alumina.

Such an operation is carried out for example at ambient temperature in a crusher made of alumina or another substance.

On variant consists in using dry-precushed alumina powder which has a specific area of about $1 \text{ m}^2/\text{g}$. This powder is put in suspension in said solvent simply by stirring and in substantially identical concentrations as used above. In this case, chloro-acetic acid is also added in concentrations such as those given above.

Whatever the method used, said solvent has the following characteristics at substantially ambient temperature.

	Viscosity	≤ 2 centipoise	
	Boiling temperature	$\geq 60^\circ\text{C}$	
15	Relative dielectric constant	≤ 22	15
	Saturated vapour pressure	$\leq 50 \text{ mm Hg}$	

The suspension is stored for example in an aluminium beaker and is constantly stirred to prevent sedimentation of the particles. A magnetic stirrer or a closed-circuit flow can be used. A deposit is then formed by electro-phoresis. To do this, a polarizable cylindrical mandrel equipped with rotation means is immersed in the beaker and a difference in potential is set up between the mandrel and the metal beaker which contains the suspension or bath, so that the particles of alumina are deposited on the mandrel. This difference in potential is such that the electric field lies between 250 and 650 volts/cm.

In the figure, the mandrel is designated by the reference 11; reference 8 designates the beaker which contains the suspension or bath 13; 9 is a magnetic stirrer driven by a motor 10. The mandrel 11 on which the deposit is to be formed is rotated with a hollow shaft 14 having a vertical axis by means of a mechanism which is not shown.

To deposit alumina particles which are contained in the suspension 13 on the mandrel 11, an electric field of about 300 volts/cm is formed between the mandrel and the beaker by means of suitable electric connections 15 and 16. 12 designates the alumina layer deposited when this field is set up. Since the distance between the outer surface of the mandrel 11 which has a diameter of 8 mm and the inside wall of the beaker 8, is about 2 centimetres, in these conditions the depositing time, i.e. the time during which the electric field is established, lies between 5 seconds and 1 minute; thus, tubes whose thicknesses lie approximately between 200μ and 3 mm may be obtained after subsequent isostatic pressure and sintering treatment.

It should be observed that in the case where the suspension is deflocculated by chloroacetic acid, the polarity of the alumina particles is negative; hence the polarity of the mandrel must be positive.

The advantage of depositing by the electro-phoresis technique of the invention is that the support or mandrel may have any shape; thus, parts other than plates or tubes may be obtained. The deposit thus obtained must then undergo isostatic compression, and it must then be suitably sintered. A finished part suitable for use directly is then obtained.

A few preferred examples of baths used by the Applicant are set forth hereinbelow to give a clearer idea of the invention:

	<i>Example 1:</i>	Methyl-propyl-ketone :	1.000 cm^3	
		Chloroacetic acid :	1.25 g	
		Beta alumina powder :	500 g	
45	Crushing in an alumina vessel	:	8 hours	45
	Deposition time	:	15 seconds	
	Electric field	:	250 volts/cm	
	Thickness of the deposit before isostatic compression:	:	2 mm	
	Thickness of the sintered tube	:	0.85 mm	
50	<i>Example 2:</i>	n-pentanol :	1.00 cm^3	50
		Chloroacetic acid :	1.25 g	
		Beta-alumina powder:	500 g	
	Crushing in an alumina vessel	:	18 hours	
	Deposition time	:	1 minute	
55	Electric field	:	400 volts/cm	55
	Thickness of the deposit before isostatic compression:	:	3 mm	
	Thickness of the sintered tube	:	1.3 mm.	

Now, as far as concerns the beta sodium alumina used, it is the beta variety and is advantageously of the type described by the Applicants in their French patent application n° 77 21 440 dated 12th July, 1977, for a method of preparing alkaline beta alumina parts.

The method of the invention therefore produces alkaline beta alumina parts with improved quality and properties by simple and inexpensive means.

Of course, the invention is not limited to the embodiments described and illustrated, which have been given only by way of example. In particular, without going beyond the scope of the invention, details can be modified, some dispositions can be changed or some means can be replaced by equivalent means.

It is also quite obvious that it would be possible to produce parts made of ceramic materials other than beta sodium alumina without thereby going beyond the scope of the invention.

Such embodiments, which would require only an adaptation of the baths to the kind of ceramic powder, could be considered only as variants within the understanding of the man in the art.

CLAIMS

1. A method of preparing ceramic parts, said method comprising the following successive stages:
 - a powder of said ceramic substance is put in suspension in a polar solvent, having the following characteristics at a temperature substantially equal to ambient temperature: a viscosity of at most 2 centipoise; a boiling temperature of at least 60°C; a relative dielectric constant which lies between 12 and 22; and a saturated vapour pressure of at most 60 millimetres of mercury.
 - a layer of ceramic substance is deposited on a mandrel or support by electrophoresis by immersing said mandrel or support in said suspension and by imparting to said mandrel or support a polarity which is the opposite of that of said powder by setting up a difference in potential between the support and, for example, the receptacle which contains said suspension,
 - said layer is dried,
 - the deposit obtained undergoes isostatic compression; and
 - the part thus obtained is sintered after the mandrel has been removed.
2. A method according to claim 1, wherein said solvent is chosen from methyl- propylketone and n-pentanol, said ceramic powder having a specific area of substantially 2 m^2 per gram and being crushed in said solvent.
3. A method according to claim 1, wherein said solvent is chosen from methyl- propylketone and n-pentanol, said ceramic powder having a specific area of 1 m^2 per gram and being previously crushed before it is put in suspension.
4. A method according to one of claims 1 to 3, wherein said ceramic powder is used in a concentration lying between 100 and 1000 g per litre of solvent.
5. A method according to any preceding claim, wherein chloracetic acid is also incorporated in said suspension at a concentration of 1 to 5 g per 1000 g of ceramic powder.
6. A method according to claim 1, wherein said difference of potential is such that the electric field lies between 250 and 650 volts/cm.
7. A method according to claim 1, wherein said ceramic substance is beta sodium alumina.
8. A method of preparing ceramic parts substantially as herein described with reference to the accompanying drawing.
9. Ceramic parts and in particular beta sodium alumina parts made by using the method according to any one of the preceding claims.